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A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1940

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NICHOLAS J. LETANG

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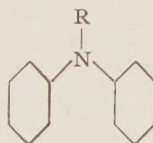
Steric Effects on the Reactivity of Aromatic Amines

BY NICHOLAS J. LETANG

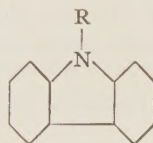
It was shown previously¹ that the acid catalyzed exchange of the ortho and para hydrogen atoms in aromatic tertiary amines is in general more or less suppressed by a substituent in one of the ortho positions. This was interpreted as primarily a steric effect and it was predicted on the same grounds that the reactivity of 1-dimethylaminonaphthalene in hydrogen exchange would be adversely affected by substituents in the 8 position. Such effects have now been observed for three substances of this type.

Further studies of the exchange reactions of

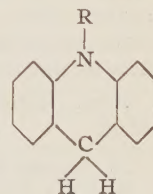
heterocyclic tertiary amines have furnished results in which the role of the steric factor is not clear. Whereas previously the activating effect of an amino nitrogen on the ortho and para hydrogen atoms was found to be greatly increased



I



II



III

R = methyl, phenyl

(1) Brown, Widiger and Letang, *J. Am. Chem. Soc.* **61**, 2597 (1939).

when the nitrogen atom forms part of a fused five or six membered ring (N-methylindoline, N-methyltetrahydroquinoline), a comparison of I with types II and III has shown an opposite result of ring closure.

Experimental

Procedure.—The essential features of the procedure for the preparation and analysis of reaction mixtures with deuterio-alcohol have been described previously.^{2,3} To guard against errors due to isotopic fractionation,⁴ all distillations of alcohol and of the water of combustion were carried out at atmospheric pressure. For each substance control determinations (no catalyst added) were carried through. These showed a small and constant decrease in deuterium concentration due to isotopic fractionation and the results obtained subsequently were corrected for this effect.

The materials used were prepared by methods described in the literature, except as noted below.

8-Nitro-1-dimethylaminonaphthalene.—8-Nitro-1-naphthylamine was prepared in 16% yield by the nitration of 1-naphthylphthalimide.⁵ Methylation with methyl sulfate produced a highly impure product which was first purified by the acetic anhydride method, then by recrystallization from alcohol, and finally by fractional sublimation in high vacuum. The pure product formed canary yellow crystals of m. p. 75°.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: N, 12.96. Found: N, 13.11.

8-Chloro-1-dimethylaminonaphthalene.—8-Chloro-1-nitronaphthalene was prepared by the chlorination of 1-nitronaphthalene,⁶ and was reduced with stannous chloride and hydrochloric acid to 8-chloro-1-naphthylamine, m. p. 88–89°. Methylation with methyl sulfate, and purification of the product by treatment with acetic anhydride, yielded 8-chloro-1-dimethylaminonaphthalene, b. p. 111–112° (4 mm.); n_D^{20} 1.6420.

Anal. Calcd. for $C_{12}H_{12}NCl$: Cl, 17.27. Found: Cl, 17.43.

1,8-Bis-dimethylaminonaphthalene.—The reduction of 1,8-dinitronaphthalene with stannous chloride and hydrochloric acid yielded 1,8-diaminonaphthalene which was methylated using 5 moles of methyl sulfate and the product was purified by treatment with acetic anhydride, b. p. 144–145° (4 mm.).

Anal. Calcd. for $C_{14}H_{18}N_2$: N, 13.08. Found: N, 12.92.

1,5-Bis-dimethylaminonaphthalene.—1,5-Dinitronaphthalene was reduced quantitatively with hydrogen using the Adams platinum catalyst. Methylation with methyl sulfate yielded a product which was refluxed with acetic anhydride for two hours, and then recrystallized from alcohol; light brown crystals, m. p. 90.5°.

Anal. Calcd. for $C_{14}H_{18}N_2$: N, 13.08. Found: N, 12.98.

N-Methylacridane.—This was prepared from methylacridinium iodide by the Decker reaction,⁷ and also by the reduction of N-methylacridone, which is a product of the Decker reaction, with sodium and amyl alcohol.⁸ The yields by the two methods are almost quantitative but the latter furnishes a better product. The substance was obtained, after crystallization from alcohol and fractional sublimation in high vacuum, as colorless crystals, m. p. 95°, which rapidly become colored on standing.

Experimental Results.—The experimental results for the acid catalyzed exchange reactions are summarized in Tables I, II and III. The analytical data reproduced in these tables refer to the concentration of deuterium in the water obtained by the combustion of the original and the recovered deuterioalcohol. The "exchange number" has been defined previously.³

TABLE I
EXCHANGE REACTIONS OF NAPHTHALENE DERIVATIVES^a

Compound, -naphthalene	% D ₂ O from alcohol		Exchange number
	Initial	Final	
1-Dimethylamino-	2.60	2.06	1.73
8-Nitro-1-dimethylamino-	2.60	2.60	0
8-Chloro-1-dimethylamino-	2.60	2.60	0
1,8-Bis-dimethylamino-	2.60	2.02	1.99
1,5-Bis-dimethylamino-	2.80	1.82	3.52

^a In these experiments, 5 cc. (0.085 mole) of deuterio-alcohol, 0.0130 mole of compound and 0.020 cc. of sulfuric acid were allowed to react at 115° for 65 hours.

TABLE II
EXCHANGE REACTIONS OF POLYNUCLEAR AROMATIC AMINES^a

Compound	% D ₂ O ^b		Exchange number
	Initial	Final	
N-Methyldiphenylamine, at 80°	2.22	1.76	
	1.67	4.48	
	1.57	5.18	
N-Methylcarbazole, at 80°	2.77	0.10	
	2.70	.27	
	2.61	.50	
N-Methylacridane, at 80°	2.76	.13	
	2.64	.44	
	2.47	.91	
Triphenylamine, at 125°	2.74	.17	
	2.64	.43	
	2.48	.89	
N-Phenylcarbazole, at 125°	2.78	.08	
	2.74	.16	
	2.69	.29	

^a The reaction mixtures consisted of 5 cc. (0.085 mole) of deuterio-alcohol, 0.0130 mole of compound, and 0.00010 mole of hydrogen chloride. For each compound three results are given; these are for reaction times of one-half, two and six hours. It was established for each compound, by experiments conducted at 115° for fifty hours, that no exchange occurred in the absence of acid.

^b Initial % D₂O for all experiments, 2.81.

(7) Pictet and Patry, *Ber.*, **35**, 2534 (1902).

(8) Bergmann, *Ann.*, **483**, 87 (1930).

(2) Kharasch, Brown and McNab, *J. Org. Chem.*, **2**, 36 (1937).

(3) Brown, Kharasch and Sprowls, *ibid.*, **4**, 442 (1939).

(4) Widiger and Brown, *J. Am. Chem. Soc.*, **61**, 2453 (1939).

(5) Hodgson and Cook, *J. Chem. Soc.*, 1844 (1936).

(6) Ferrero and Caffisch, *Helv. Chim. Acta*, **11**, 806 (1928).

TABLE III
LIMITING VALUES OF EXCHANGE NUMBERS^a

Compound	Exchange number	Active H atoms, theor.
N-Methyldiphenylamine	5.22	6
N-Methylcarbazole	3.38	4
N-Methylacridane	3.41	4
Triphenylamine	7.71	9
N-Phenylcarbazole	5.93	7

^a These were determined by experiments in which mixtures of 5 cc. of deuterioalcohol, 0.0130 mole of compound, and 0.068 g. of sulfuric acid were allowed to react at 115° for fifty hours. Under these conditions the exchange reactions in each case reached virtual equilibrium. The theoretical number of active hydrogen atoms is based on the assumption that only hydrogen atoms ortho or para to a nitrogen atom are active.

N-Methylacridane was also investigated with regard to a base catalyzed hydrogen exchange reaction. The following experiment is typical. A mixture of 1.95 g. of N-methylacridane, 5 cc. (0.085 mole) of deuterioalcohol, and 0.0020 g. of sodium hydroxide was heated in an evacuated sealed tube at 110° for ninety-five hours. The original deuterioalcohol on combustion yielded 2.80% D₂O, the recovered alcohol yielded 2.56% D₂O. The decrease corresponds to an exchange of 0.79 hydrogen atom. In the absence of acid and base no exchange was observed.

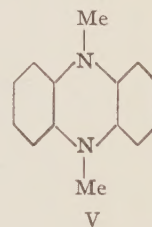
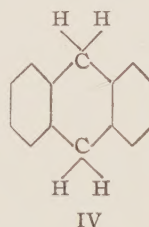
Discussion

The results for 1-dimethylaminonaphthalene and peri substituted derivatives (Table I) show decisively the loss of reactivity accompanying this type of substitution. Bearing in mind that the limiting value for the exchange number, according to our previous results (*cf.* also Table III), is about 15% less than the actual number of hydrogen atoms reacting, it will be noted that the reaction of 1-dimethylaminonaphthalene is practically at equilibrium while there has been no measurable reaction of the peri nitro and chloro derivatives. The mutual hindrance of two dimethylamino groups is seen in the lower rate of reaction of the 1,8 compound (60% complete for the exchange of four hydrogen atoms for the conditions given) as compared with the 1,5 compound (complete exchange for four hydrogens). These results lie within the framework of the theory of steric effects previously outlined.^{1,3} Supporting evidence based on reactivity in other types of substitution reactions appears to be not yet available, but doubtless the "peri" effect will prove to be as characteristic as is the "ortho" effect.

For the variations in exchange reactivity in the series of diphenylamine and carbazole derivatives, the steric factor is evidently subordinate. The lower reactivity of carbazole derivatives⁹ notwithstanding the favorable planar structure, is probably a consequence of the additional resonance stabilization of the pyrrole ring which would have to be overcome in the formation of a quinonoid intermediate.

The hydrogen exchange of N-methylacridine is subject to catalysis by both acids and bases. The active hydrogens in the base catalyzed reaction are doubtless the methylene hydrogen atoms, and the rate of the reaction is of the same order of magnitude (actually three times greater for identical experimental conditions) as that previously observed for xanthene¹⁰ which is structurally analogous. The acid-catalyzed reaction involves the four hydrogen atoms which are ortho or para to the nitrogen atom as is shown by the observed limiting value for the exchange number (Table III).

The rate of the acid catalyzed reaction is very much smaller than the rate for N-methyldiphenylamine. In the absence of any conceivable electronic effects which could account for it, this result points to the conclusion that N-methylacridane does not have a planar structure. N-Methylacridane (III, R = Me) resembles dihydroanthracene (IV) and N,N'-dimethyldihydrophenazine (V), for both of which a structure folded



about a central axis is considered probable by Campbell and co-workers¹¹ who have summarized the experimental evidence. A similarly folded structure for N-methylacridane might account for our results.¹²

(9) Similar differences are to be seen in the condensation reactions of N-diphenylamine and N-methylcarbazole with aldehydes (Sen and Sen, *J. Indian Chem. Soc.*, **7**, 965 (1930), as well as in ordinary substitution reactions, the former substance being much more reactive.

(10) Heuse, Master's Dissertation, University of Chicago, 1937.

(11) Campbell, LeFèvre, LeFèvre and Turner, *J. Chem. Soc.*, 404 (1938).

(12) Strictly speaking, the question in our case revolves about the configuration of the quinonoid amine salt (or cation) and this, whether folded or planar, would be a strained structure.

Summary

1. The acid catalyzed hydrogen exchange reaction of 1-dimethylaminonaphthalene is greatly retarded by a chloro or nitro group in the 8 position. 1,8 - Bis - dimethylaminonaphthalene exchanges hydrogen more slowly than the 1,5 isomer. These observations support a mechanism previously advanced.

2. Carbazole and acridane derivatives are less reactive in hydrogen exchange than the corresponding diphenylamine derivatives. The role of steric factors is discussed.

3. N-Methylacridane also exhibits a base catalyzed exchange reaction which is thought to involve the methylene hydrogen atoms.



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